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Manufacture of Alcohol, &c.

LETTERS PATENT to John Henry Johnson, of 47, Lincoln's Inn Fields, in the County of Middlesex, Gentleman, for an Invention of "IMPROVEMENTS IN THE MANUFACTURE OF ALCOHOL, AND IN THE UTILISATION OF RESIDUAL PRODUCTS FROM SUCH MANUFACTURE." A communication from abroad by Eugène Porion and Louis Mehay, of Wardrecques, Nord, in the Republic of France.

PROVISIONAL SPECIFICATION left by the said John Henry Johnson at the Office of the Commissioners of Patents on the 3rd July 1880.

JOHN HENRY JOHNSON, of 47, Lincoln's Inn Fields, in the County of Middlesex, Gentleman. "IMPROVEMENTS IN THE MANUFACTURE OF ALCOHOL, AND IN THE UTILISATION OF RESIDUAL PRODUCTS FROM SUCH MANUFACTURE." A communication from abroad by Eugène Porion and Louis Mehay, of Wardrecques, Nord, in the Republic of France.

This Invention relates to the manufacture of alcohol, and it has for its object the utilization of the residues resulting from the treatment with acids of amylaceous substances employed in this manufacture, that is to say, all descriptions of amylaceous grain and fruit, such, for example, as ric, barley, rye, oats, and other sereals, beans, and other vegetables, chesnuts, acorns, almonds, pips, and the like.

The Invention consists essentially in the use of the means hereinafter described for obtaining in the treatment of grain by saccharification with acids, liquid, pasty, or solid residues adapted for feeding cattle, and is highly concentrated as possible with a view to increasing their nutritious qualities; and in particular the Invention comprises,—

1st. The employment of hydro chloric acid purified either by means of salts of baryta or any other suitable means calculated to reduce the proportion of sulphuric acid which it contains when in a crude condition in effecting the saccharification of grain and the employment of carbonate of soda, either entirely or approximately free from sulphate for saturating the said acid, all with a view to improving the quality of the liquid residue.

2ndly. Obtaining by the means hereinbefore described cakes of residue of grain (in the treatment of the latter by acids) with or without preliminary extraction

of the oil which they contain, the said cakes when made from grain containing oil, constituting a novel product adapted for use in or supplying oil works.

In carrying out this Invention in order to obtain liquid residues suitable for food for cattle it is proposed to adopt the treatment next hereinafter described.

With a view to rendering the residues resulting from the treatment of grain or other analogous substances with acids, and especially hydrochloric acid, available as food for cattle, it has been proposed to saturate the hydrochloric acid usually employed in this treatment with carbonate of soda, but it was found that the residues so obtained did not possess all the qualities desired chiefly on account of the large proportion of sulphuric acid which is generally present in the hydro chloric acid of commerce, and that the unpurified carbonate of soda employed for the saturation contained a considerable proportion of sulphate of soda, which rendered the residue thus obtained in a high degree relaxing.

Now according to this Invention this disadvantage is obviated by employing perfectly pure carbonate of soda, and purifying the hydrochloric acid of commerce by means of a solution of chloride of barium obtained by submitting natural carbonate of baryta in a granular condition or in lumps to the action of weak hydrochloric acid, marking from about 6 to 8 degrees Beaumé.

In order to effect the purification of the acid two vessels, hereinafter designated No. 1 & No. 2, are employed, the said vessels being of equal dimensions, and furnished with a cock situate at a short distance from the bottom for the escape of the clear liquid, a plug being provided at the lowest part for the escape of the deposit.

The vessel No. 1 is about half filled with water; about an equal quantity of the acid to be purified is then added, and the solution of chloride of barium is introduced in sufficient quantity, so that the liquid after settling yields only a very small quantity of precipitate on the addition of a fresh quantity of the reagent. The contents of the vessel are then allowed to settle, and the clear liquid thus obtained may be employed in the process of saccharification.

When the vessel has been emptied to the level of the cock it is refilled with water, and the precipitate sulphate of baryta is caused to be held in suspension in order to wash it, after which it is allowed to settle, and in the mean time preparations are made for purifying in the vessel No. 2 in the same manner as described with reference to vessel No. 1. If considered necessary the precipitate may be washed several times by the same means.

The water employed in the washing may, after settling, be employed in the saccharification as first water, and the sulphate of baryta obtained may be employed as a pigment or for the preparation of various chemical products.

What is known as purified hydrochloric acid of commerce, that is to say, the acid which is collected in the last condensing receivers may also be employed, but in general it will be found to be cheaper and safer to purify the acid as hereinbefore described.

In order to increase the density of the residue obtained by operating with the acid, wort or must of considerable density, by preference, are caused to ferment so as to obtain a wine containing, say, from about 5 to 6 per cent. of alcohol, which object may be effected without inconvenience by imparting to the must a degree of acidity equivalent to from about 15 to 30 grains of sulphuric acid per quart.

In this case it is also necessary to provide effectual means for cooling, as it is not possible to add a large quantity of cold water in order to lower the temperature, since if the cooling occupies too much time an acid fermentation would be liable to take place.

The small quantity of free acid remaining in the dregs or residue is not injurious to cattle, but the saturation may be completed by means of a small quantity of carbonate of soda before allowing them to eat it.

When it is desired to obtain solid residues available as food for cattle or as manure, the treatment next hereinafter described is adopted.

In case it is not possible to utilise the liquid residues as food for cattle, it is

more economical to effect the saturation by means of chalk in the manner ordinarily employed, and the purification of the hydrochloric acid may then be dispensed with.

It will however be found advantageous in this case to treat the solid residue of distillers' wash as hereinafter described in order to utilise it as food for cattle.

For this purpose it is necessary, first, either to separate the wash from the sand, resulting principally from the chalk employed, or avoid its introduction during the process; secondly, to separate the liquid from the organic matter in suspension; and, thirdly, to free this matter from the chloride of calcium resulting from the saturation of the hydrochloric acid with chalk.

The first of these operations, *viz*t., the elimination of the sand, may be effected either by allowing the wines to stand and settle in suitable vessels or reservoirs or upon inclined trays, or by previously purifying the milk of chalk employed by the ordinary methods and carefully washing the grain.

The second operation, *viz*t., separating the organic matter in suspension, may be effected by passing the distillers' wash through filter presses, and the liquid residues from the operation are then employed for irrigation after being cooled to below 40° centigrade in reservoirs, in which it is advantageous to add lime in order to neutralise the clear parts of the wash. In this case if the liquid is allowed to settle a deposit may be collected, forming a manure extremely rich in phosphate of lime. The lime may be added to the thick or muddy liquid before it is passed through the filter press when it is desired to retain the phosphate of lime in the cakes obtained as hereinafter described.

According to another method the liquid residues are evaporated and treated with lime in order to form solid manure.

The third operation, *viz*t., the elimination of the chloride of calcium, is effected by simply taking the solid matter issuing from the filter presses and pressing it again under screw presses, or by preference under hydraulic presses, and thereby manufacturing it into cakes of residue or dregs, which after being stove dried may be employed either for feeding cattle or as manure. According to another method the chloride of calcium may be extracted by a washing process, the matter taken from the filter presses being diluted with water and then passed again through the same apparatus, or through other filter presses provided for the purpose.

After eliminating the chloride of calcium as described, the cakes thus obtained are dried either in the open air or by means of heated air in stoves.

The processes next hereinafter described relate to extraction of the oleaginous matter.

When the crude material treated in distilling consists of maize or other grain containing oil, it is desirable to extract the oil contained in the cakes of residue obtained as hereinbefore described. For this purpose the said cakes are first pulverised when in a dry condition by means of vertical grinding mills, or when in a wet condition by means of rasps, such as are used in fecula works, in which case the desiccation is completed by passing the rasped product through heaters, such as are used in oil works, or through suitable drying apparatus; the dried product should then contain from ten to 20 per cent. of water.

The oleaginous flour thus obtained may then be submitted directly to the action of an oil press after being again dried.

The product in the form of cakes, or powder of residue, or dregs obtained as hereinbefore described, is capable of being stored without deterioration, and may be sold as crude material to oil manufacturers.

The cakes obtained after the oil has been extracted are also not liable to deterioriation, and may be sold or used as food for cattle or as manure.

When the grain employed is rich in oil, the wash obtained by the second pressing of the wet cakes carries away with it a small quantity of oil which may be readily collected by means of an intermediate reservoir, acting as an analyser, that is to

say, provided with an outlet pipe in the form of a syphon, and from which the oil may be drawn off as it accumulates by means of a suitable draw off cock.

This extraction of the oil is rendered possible since it has been ascertained that in the muliple operations of the manufacture of alcohol (saccharification, fermentation, distilling) the oil contained in the grain constantly remains attached to the undissolved solid parts, so that after the starch has disappeared this solid matter frequently contains ten times more oil than the grain employed.

In lieu of effecting the separation of the solid matter from the wash, as hereinbefore described, this separation may be effected in the wines, musts, or worts after fermentation, which affords the advantage of yielding a clear liquid for the purposes of distillation.

According to another method the separation of the solid matter and the extraction of the oil which it contains may be effected immediately after the sacchrification of the grain. This method will be found especially advantageous when it is desired to produce yeast from clear wort.

In this case grain may be submitted to sacchrification when in an entire or slightly bruised condition as is well known, and the clear wort for fermentation may be extracted by washing.

The solid matter after being sufficiently exhausted by water is pressed and treated in the same manner as the solid residue resulting from the distillers' wash. The liquid collected is caused to return to the livigator as wash water.

The improved treatment is also applicable to tender amylaceous fruits, such for example, as horse chesnuts, which are thereby caused to yield as residues an oil of considerable value for medicinal purposes, and cakes of good quality for cattle. In this case the fruit should be slightly bruised between cylinders before being submited to the treatment.

The improved system of treatment hereinbefore described thus enables a product adapted for feeding cattle to be obtained in an economical manner from residues resulting from the manufacture of alcohol from grain by means of acids; the process is however also applicable to the utilisation of the residues resulting from the treatment of grain in the process of malting. In the case of maize and other oleaginous grain, the improved treatment enables the oil remaining in the residues to be extracted, while at the same time improving the quality of the latter.

SPECIFICATION in pursuance of the conditions of the Letters Patent filed by the said John Henry Johnson in the Great Seal Patent Office on the 3rd January 1881.

JOHN HENRY JOHNSON, of 47, Lincoln's Inn Fields, in the County of Middlesex, Gentleman. "IMPROVEMENTS IN THE MANUFACTURE OF ALCOHOL, AND IN THE UTILISATION OF RESIDUAL PRODUCTS FROM SUCH MANUFACTURE." A communication from abroad by Eugene Porion and Louis Mehay, of Wardrecques, Nord, in the Republic of France.

The said Invention relates to the manufacture of alcohol, and it has for its object the utilization of the residues resulting from the treatment with acids of amylaceous substances employed in this manufacture, that is to say, every description of amylaceous grain and fruit, such, for example, as rice, barley, rye, oats, and other cereals, beans, and other vegetables, chesnuts, acorns, almonds, pips, and the like.

With a view to rendering the residues resulting from the treatment of grain or other analagous substances with acids, and especially hydrochloric acid, available as food for cattle, it has been proposed to saturate the hydrochloric acid usually employed in this treatment with carbonate of soda, but it was found that the residues so obtained did not possess all the qualities desired, chiefly on account of the large proportion of sulphuric acid which is generally present in the hydrochloric acid of commerce, and also by reason of the unpurified carbonate of soda employed for the saturation containing a considerable proportion of sulphate of soda, which rendered the residue thus obtained in a high degree relaxing.

Now, according to this Invention, disadvantage is obviated by employing pure carbonate of soda and purifying the hydrochloric acid of commerce by means of a solution of chloride of barium obtained by submitting natural carbonate of baryta in a granular condition or in lumps to the action of weak hydrochloric acid, marking from about six to eight degrees Beaumé.

In order to effect the purification of the acid two vessels, hereinafter designated No. 1 and No. 2, are employed, which vessels are of equal dimensions, and furnished with a cock or valve situate at a short distance from the bottom for the escape of the clear liquid, a plug being provided at the lowest part for the escape of the deposit.

The vessel No. 1 is about half filled with water, about in equal quantity of the acid to be purified is then added, and the solution of chloride of barium is introduced in sufficient quantity so that the liquid, after settling, yields only a very small quantity of precipitate on the addition of a fresh quantity of the reagent. The contents of the vessel are then allowed to settle, and the clear liquid thus obtained may be employed in the process of saccharification.

When the vessel has been emptied to the level of the cock it is refilled with water, and the precipated sulphate of baryta is caused to be held in suspension in order to wash it, after which it is allowed to settle, and in the meantime preparations are made for purifying in the vessel No. 2 in the same manner as described with reference to vessel No. 1. If considered necessary the precipitate may be washed several times by the same means.

The water used in the washing may, after decantation, be employed in the saccharification as primary water, and the sulphate of baryta obtained may be employed as a pigment or for the preparation of various chemical products.

What is known as purified hydrochloric acid of commerce, that is to say, the acid which is collected in the last condensing receivers may also be employed, but in general it will be found to be cheaper and safer to employ acid specially prepared or purified for this purpose.

In order to increase the density of the residue obtained by operating with the acid wort or must of considerable density is by preference employed, the same being caused to ferment so as to obtain a wine or liquid containing, say, from about five to six per cent. of alcohol, which object may be effected without inconvenience by imparting to the wort or must a degree of acidity equivalent to, say, from about fifteen to thirty grains of sulphuric acid per quart.

In this case it is also necessary to provide effectual means for cooling, as it is not possible to add a large quantity of cold water in order to lower the temperature, since, if the cooling occupies to much time, an acid fermentation would be liable to take place.

The small quantity of free acid remaining in the dregs or residue is not injurious to cattle, but the saturation may be completed by means of a small quantity of carbonate of soda before allowing them to eat it.

When it is desired to obtain the residues in a solid form, available as food for cattle or as manure, the treatment next hereinafter described is adopted.

In case it is not possible to utilise the liquid residues as food for cattle it is more economical to effect the saturation by means of chalk in the manner ordinarily employed, and the purification of the hydrochloric acid may then be dispensed with. It will however always be found advantageous to treat the solid residue of distillers' wash, as hereinafter described, in order to utilise it as food for cattle.

For this purpose it is necessary first, either to separate the wash from the sand, resulting principally from the chalk employed, or avoid its introduction during the process; secondly, to separate the liquid from the organic matter in suspension; and, thirdly, to free this matter from the chloride of calcium resulting from the saturation of the hydrochloric acid with chalk.

The first of these operations, *videlicet*, the elimination of the sand may be effected either by allowing the wines or liquids to stand and settle in suitable vessels or tanks, or upon inclined trays, or by previously purifying the milk of chalk employed by the ordinary methods and carefully washing the grain.

The second operation, *videlicet*, separating the organic matter in suspension may be effected by passing the wash through filter presses, and the liquid residues from the operation are then employed for irrigation after being cooled to below forty degrees centigrade in reservoirs in which it is advantageous to add lime in order to neutralise the clear parts of the wash; in this case, if the liquid is allowed to settle a deposit may be collected, forming a manure very rich in phosphate of lime. This saturation with lime may be performed on the thick or muddy liquid before it is passed through the filter press when it is desired to retain the precipitated phosphate of lime in the cakes obtained, as hereinafter described.

According to another method the liquid residues are evaporated and treated with lime in order to form solid manure.

The third operation, *videlicet*, the elimination of the chloride of calcium, is effected by simply taking the matter discharged from the filter presses and pressing it again under screw presses, or by preference under hydraulic presses, and thereby manufacturing it into cakes of residue or dregs, which, after being stove dried, may be employed either for feeding cattle or as manure. According to another method the chloride of calcium may be extracted by a washing process, the matter taken from the filter presses being first diluted with water, and then passed again through the same apparatus or through other presses or filter presses provided for the purpose.

After eliminating the chloride of calcium as described, the cakes thus obtained are dried, either in the open air or by means of heated air in stoves.

The processes next hereinafter described relate to the extraction of the oleagenous matter.

When the crude material treated in distilling consists of maize or other grain containing oil, it is desirable to extract the oil contained in the cakes of residue obtained, as hereinbefore described. For this purpose the said cakes are first

pulverised when in a dry condition by means of vertical grinding mills, or when in a wet condition by means of rasps, such as are used in fecular works, in which case the desiccation is completed by passing the rasped product through heaters, such as are used in oil works, or through suitable drying apparatus for treating pulverised matter; the dried product should then contain, say, from ten to twenty per cent. of water.

The oleagenous flour thus obtained may then be submitted directly to the action of an oil press after being again heated.

The product consisting of residue or dregs in the form of blocks or powder, obtained as hereinbefore described, is capable of being stored without deterioration, and may be sold as crude material to oil manufacturers.

The cakes obtained after the oil has been extracted are also not liable to deterioration, and may be sold or used as food for cattle or as manure.

When the grain employed is rich in oil, the wash expressed from the moist blocks by the second pressing carries away with it a small quantity of oil, which may be readily collected by means of an intermediate reservoir acting as an analyser, that is to say, provided with an outlet pipe in the form of a syphon, and from which the oil may be decanted as it accumulates by means of a small valve.

This extraction of the oil, as hereinbefore described, is rendered possible since it has been ascertained that in the multiple operations of the manufacture of alcohol (saccharification, fermentation, distilling) the oil contained in the grain constantly remains attached to the undissolved solid parts, so that after the starch has disappeared this solid matter frequently contains ten times more oil in proportion than the grain employed.

In lieu of effecting the separation of the solid matter from the wash, as hereinbefore described, this separation may be affected in the wines, must, or wort after fermentation, which method affords the advantage of yielding a clear liquid for the purpose of distillation. In this mode of proceeding however the product is more liable to become deteriorated, and thereby prejudice the yield of alcohol.

According to another method, the separation of the solid matter and the extraction of the oil which it contains may be affected immediately after the saccharification of the grain. This method will be found especially advantageous when it is desired to produce yeast in the treatment of clear wort.

In this case the grain may be submitted to saccharification when in an entire or slightly bruised condition, as is well known, and the clear wort for fermentation may be extracted by washing.

The solid matter after being sufficiently exhausted by water is pressed and treated in the same manner as the solid residue resulting from the distillers' wash. The liquid collected is caused to return to the levigator as wash water.

The improved treatment is also applicable to tender amylaceous fruits, such for example, as horse chesnuts, which are thereby caused to yield as residues an oil of considerable value for medicinal purposes, and cakes of good quality for cattle. In this case the fruit should be slightly bruised between cylinders before being submitted to the treatment.

The important feature of the improved system of treatment hereinbefore described thus consists in enabling a product adapted for feeding cattle to be obtained in an economical manner from residues resulting from the manufacture of alcohol from grain by means of acids; the process is however also applicable to the utilisation of the residues resulting from the treatment of grain in the process of malting. In the case of maize and other oleagenous grain, the improved treatment also enables the oil remaining in the residues to be extracted, while at the same time improving the quality of the latter.

Having now described and particularly ascertained the nature of the said Invention, and the manner in which the same is or may be used or carried into effect, I would observe in conclusion that what I consider to be novel and original

and therefore claim as the Invention secured to me by the hereinbefore in part recited Letters Patent is,—

First. The means, substantially as hereinbefore described, for obtaining in the treatment of grain by saccharification with acids, liquid, pasty, or solid residues adapted for feeding cattle, and as highly concentrated as possible, with a view to increasing their nutritious qualities.

Second. The employment in effecting the saccharification of grain of hydro chloric acid, purified either by means of salts of baryta or any other means calculated to reduce the proportion of sulphuric acid which it contains when in a crude condition, and also the employment of carbonate of soda, either entirely or approximately free from sulphate, for saturating the said acid, all with a view to improving the quality of the liquid residue, substantially as hereinbefore described.

Thirdly. The production by the means substantially as hereinbefore described from the residue of grain of cakes available as food for animals, with or without preliminary extraction of the oil contained therein, the said cakes when made from grain containing oil constituting a new product adapted for use in or supplying oil works, substantially as hereinbefore described.

In witness whereof, I, the said John Henry Johnson, have to this my Specification set my hand and seal, the Thirty first day of December, One thousand eight hundred and eighty.

J. HENRY JOHNSON. (L.S.)

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